

Research Article

Kinetic Study and Thermodynamics of a Medicinal Plant: The Eucalyptus Camaldulensis

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Abstract

A medicinal aromatic plant "Eucalyptus Camaldulensis" was studied in order to study its properties thermodynamics and hygroscopic. The purpose of this study is to characterize (preservation and transformation) the product. Several drying experience were carried out in terms of kinetics of drying (kinetic study) and isotherms of sorption (thermodynamic study). It turns out that we have to present the equipments and the used methods.

Keywords: drying, Eucalyptus Camaldulensis, isotherms of sorption, modeling, essential oil.

1. Introduction

The aromatic and medicinal plants, which are produced in many countries in the industrial world under very varied forms, are an inexhaustible spring of molecules. Molecules stemming from these plants are often likened to active ingredients possessing specific properties which confer them an only character. Stemming from the biodiversity, these particularities looked for plants are adapted to countries among which the environment and the climate facilitate their culture. The exploitation (operation) of the molecules is possible only in the countries where the population maintains and cultivates these plants for decades.

However, the factor limiting the valuation of these products, especially in terms of preservation and transformation (processing), is their rather high (high enough) humidity (until 75 %). (Cháfer, M et al, 2003; Aidi Mohamed, L, (2006) ; Singh, K et al, 2006)).

The impact of the water in interaction with the other constituents of the product can be approached either by its moisture content or by the activity of the water which quantifies the energy of connection with the dry material of the product. The physical mechanisms which check the transfers of mass and heat inside the product are diverse. They depend of characteristics of the product, in particular its structure and its composition but also the processes of drying used to generate these transfers. In front of such a complexity, to resort to the experiment before the conception of an industrial process seems to be necessary to determine the hygroscopic properties of the product in question with the aim of a better

preservation during the storage and a good behavior of the operation of drying. This present study consists in this frame in preservation and transformation of healing plants. It consists in three parts:

- A thermodynamics study: the isotherms of sorption were determined by the gravimetric method for three temperatures (40, 50 and 60°C). These isotherms were adjusted by eight mathematical models.
- The second part concerns the study of the kinetics of convective drying of Eucalyptus Camaldulensis at five levels of temperatures (30, 40, 50, 60 and 70°C). 11 mathematical models of drying were tested for the smoothing of the kinetics of drying of Eucalyptus Camaldulensis.
- The last study was dedicated to the study of the effect of the temperature of drying on the efficiency and the quality of essential oil extracted from Eucalyptus Camaldulensis.

2. Materials and method

1) Isotherms of sorption

In this study, we opted for the method static gravimétrique to determine the isotherms of sorption of Eucalyptud Camaldulensis. The principe of the static method consists in putting the samples of leaves to be adsorbed or desorbed in hermetic surrounding walls containing the solutions saturated in salts until reach the balance thermodynamics in a atmosphere that the temperature and the relative humidity are maintained constants. This method is slow; it lasts several days and even weeks. The experimental device consists of

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Table 2: Models of description of the isotherms of sorption (Y.Jannot, 2006)

Model	Equation	Domain of validity
Langmuir	$X_{\acute{e}q} = \frac{A \cdot B \cdot Hr}{1 + Hr}$	Faibles HR
BET	$X_{\acute{e}q} = \frac{(A + B \cdot T) \cdot C \cdot Hr}{(1 - Hr)(1 - Hr + C \cdot Hr)}$	HR < 50
GAB	$X_{\acute{e}q} = \frac{A \cdot B \cdot C \cdot Hr}{(1 - B Hr)(1 - (1 - C) B Hr)}$	10 < HR < 90
Chung-Pfost	$A_w = \exp \left[\frac{-A}{T + B} \cdot \exp(-C \cdot X_{\acute{e}q}) \right]$	20 < HR < 90
Peleg	$X_{\acute{e}q} = A \cdot Hr^{k_1} \cdot Hr^{k_2}$	HR < 50
Smith	$X_{\acute{e}q} = A - B \cdot \ln(1 - Hr)$	50 < HR < 95
Oswin	$X_{\acute{e}q} = (A + B \cdot T) \cdot \left[\frac{Hr}{1 - Hr} \right]^C$	10 < HR < 90
Henderson	$1 - Hr = \exp(-A(T + B) \cdot X_{\acute{e}q}^C)$	50 < HR < 95

the use of nine jars filled approximately in the quarter of nine saturated solutions of salts. (KCL, MgCl₂, NaBr, NaCl, BaCl₂, NaNO₃, K₂CO₃, KOH, KI). (B. Kammoun et al, 2012)

These solutions allow to obtain values of activity varying from 0.109 to 0.891.

The sample is suspended in the jar, over salts, and thus stays in an atmosphere stabilized in temperature and in hygrometry. The experience is realized for three temperatures 40, 50 and 60°C. The follow-up of the losses of mass for the adsorption and the earnings of mass for the desorption is assured by a precision balance ± 0,001 g. The hygroscopic balance is obtained when the exchange between the product and the ambient air is ended. As soon as the wet masses are determined, samples are introduced into a steam room in 105°C during 12 pm to determine their dry masses. The product undergoes a predrying to undergo the phenomenon of adsorption. The predrying is realized in a steam room carried in a temperature of 50°C and this until maximal dehydration of the product. (H. Bizot et al, 1981)

2) Kinetics of drying

For this experience we used as working tools a steam room working in atmospheric pressure and allowing to make diverse heat treatments with temperatures regulated (30, 40, 50, 60 and 70°C). For every temperature, we put a known mass (5g), we follow its variation during weather until the difference of mass becomes of the order of 0,001 meadow. The same sample is put in the steam room in 105°C during 24 hours what allows us to determine the dry mass.

3) Extraction of essential oil

The objective of this study is the determination of the optimal temperature of drying to obtain an efficiency raised with better quality.

At the end to extract essential oil, the sheets (leaves) of Eucalyptus have sudden a hydrodistillation

during 3 am. The floral water containing essential oil was mixed with an organic solvent (the ether diéthylique) in a bulb in settled.

The essential oil Obtained, was finally kept (preserved) in dark flasks and hermetically closed in 4°C for the later analyses

To follow the quality of essential oil by determining their chemical compositions, we proceeded by the method chromatography in gas phase coupled with a spectroscopy of mass (CPG/SM).

4) Modeling of the curves of sorption

The last stage of the study of isotherms consists in a modeling of the curves of adsorption and of desorption, to end in an adequate mathematical equation. In this work we chose the following eight models.

The coefficient of correlation (r) is one of the first criteria to plan the best equation which describes the isotherms of sorption. Besides r, the relative average error (EMR) and the standard error of the humidity (ESH) are used in the same objective. These statistical parameters are calculated as follows:

$$EMR = \frac{100}{N} \sum_{i=1}^N \left| \frac{X_{\acute{e}q, \text{exp}} - X_{\acute{e}q, \text{pre}}}{X_{\acute{e}q, \text{exp}}} \right|$$

$$ESH = \sqrt{\frac{\sum_{i=1}^N (X_{\acute{e}q, \text{exp}} - X_{\acute{e}q, \text{pre}})^2}{d}}$$

5) Modeling of curves of kinetics of drying

The modeling of the curves of drying is defined by the equation: X = f (t) said characteristic equation of drying. We find in the literature an abundance of mathematical models in the form of the empirical or semi-empirical relations to describe the curves of kinetics of drying. The different equations give the evolution during drying of the moisture content of balance according to time. These equations contain

Table 1: Mathematical models of drying (T.L.Togrul& D.Pehlivan, 1971)

Model	Expression of the model
Newton	$X = \exp(-kt)$
Page	$X = \exp(-kt^n)$
Page modifié I	$X = \exp(-(kt)^n)$
Page modifié II	$X = \exp((-kt)^n)$
Henderson et Pabis	$X = a \exp(-kt)$
Logarithmique	$X = a \exp(-kt) + c$
Modèle Exponentiel à deux termes	$X = a \exp(-k_0t) + b \exp(-k_1t)$
Modèle Exponentiel modifié à deux termes	$X = a \exp(-kt) + (1-a) \exp(-kat)$
Wang et Singh	$X = 1 + at + bt^2$
Henderson et Pabis modifié	$X = a \exp(-kt) + b \exp(-gt) + c \exp(-ht)$
Midilli-Kucuk	$X = a \exp(-kt^n) + bt$

constants which are adjusted to suit to the experimental curves of drying. Consequently, they are valid only in the field of experimental study for which they were established. The table1 groups some characteristic equations of drying found in the literature to describe the kinetics of sun drying in thin layer of a product (S.Simal, 1947; B. Touati, 2008).

3. Results and discussion

1) Isotherms of sorption

The hygroscopic balance of Eucalyptus Camaldulensis is reached at the end of twenty days for the adsorption and twenty six days for the desorption. Figure1, 2 and 3 show respectively the experimental results obtained for the adsorption and for the desorption of Eucalyptus for the temperatures 40, 50 and 60°C. According to these figures, we notice that the curve of adsorption is superior to that of desorption and that the moisture content X_{eq} is an increasing function of the activity. The curve of adsorption does not overlap with the curve of desorption, highlighting a phenomenon of hysteresis. (T.L.Togrul& D.Pehlivan, 1971).

By basing itself on the various results of the modeling of the isothermal curves, one notice that the model of GAB is the best model to describe all the isotherms of adsorption and of desorption of Eucalyptus for all the values of studied temperatures. This model still possesses the advantage to be valid on a wide range of relative humidity (from 0,05 to 0,9). The isotherms of desorption and of adsorption of Eucalyptus Camaldulensis moderated and calculated by the model of GAB (the most adequate model) for the temperature 40, 50 and 60°C are presented in figures 4,5.

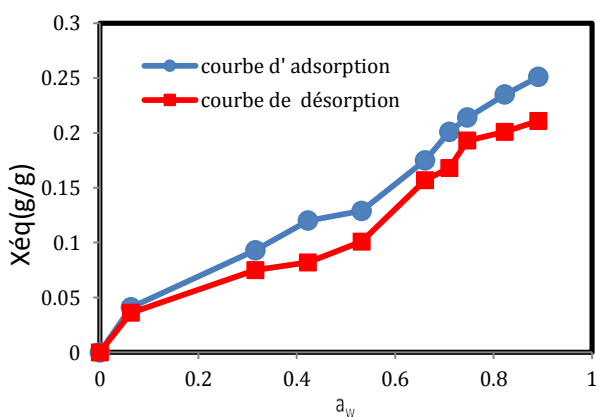


Fig 1: Isotherms of adsorption and of desorption of eucalyptus foT=40°C

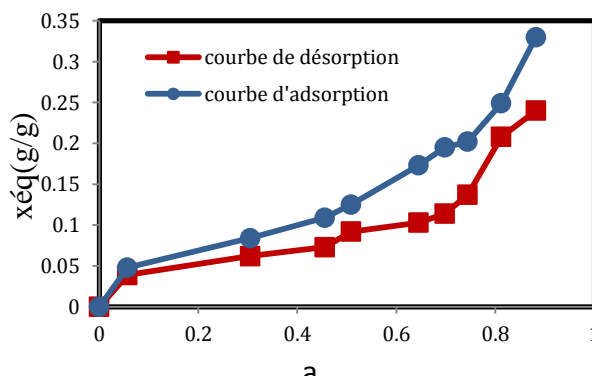


Fig 2: Isotherms of adsorption and of desorption of eucalyptus for T=50°C

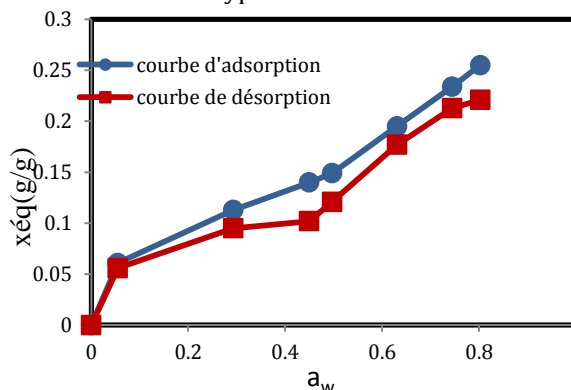


Fig 3: Isotherms of adsorption and of desorption of eucalyptus for T=60°C

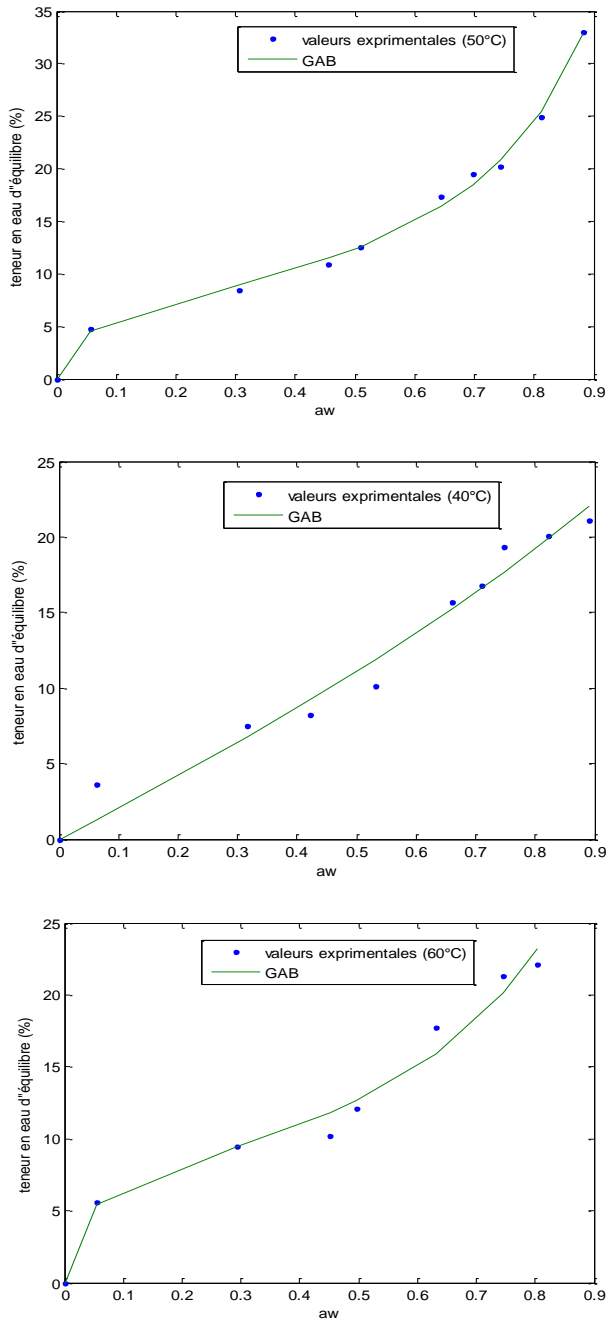


Fig 4: Curves of desorption calculated by the model of GAB in different temperatures

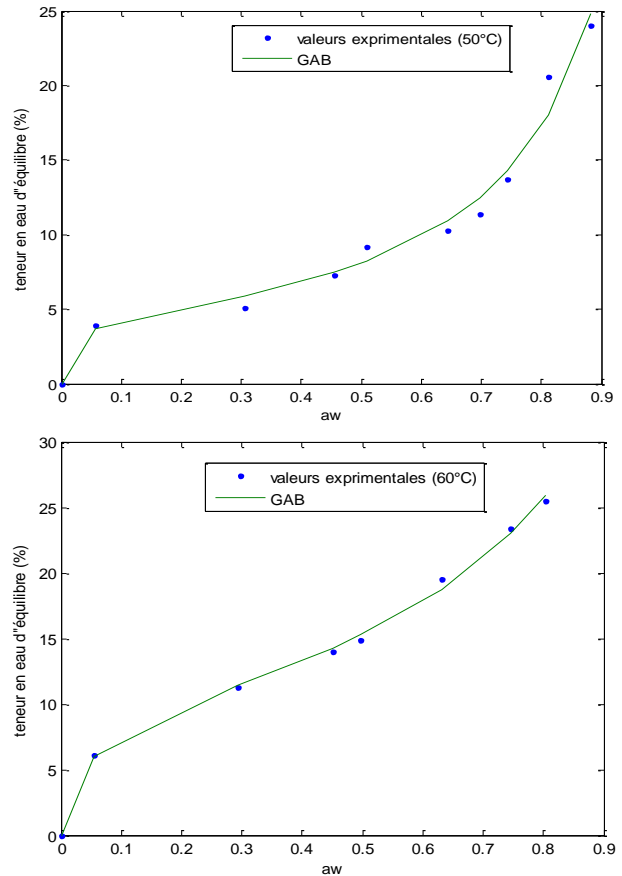
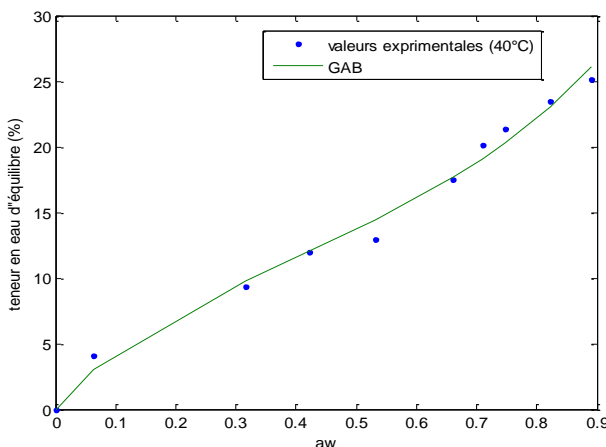


Fig 5: Curves of adsorption calculated by the model of GAB in different temperatures

2) Kinetics of drying

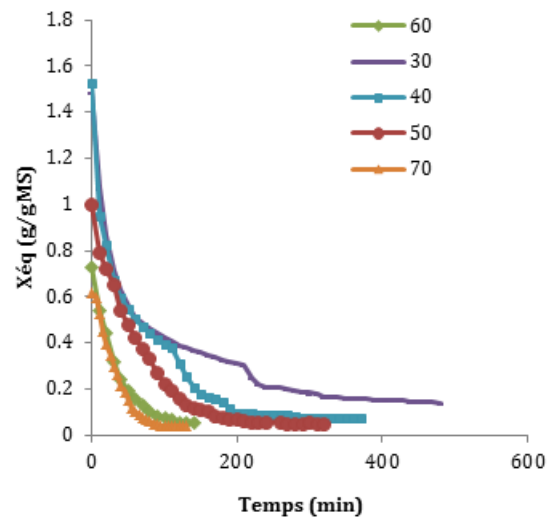


Fig 6: Evolution of the moisture content according to time: effect of the temperature

We notice, according to this figure, that when the temperature increases the time of drying and the moisture content decrease.

Quite as for the modeling of the isotherms of sorption, the choice of the most adequate model is based on the highest coefficient of correlation. We found that the model of Page is the best model to describe the kinetics of drying for an equal

Table 6: main chemical compounds of essential oil

Compounds	Percentage (%)						
	Temperature T (°C)						
	30	40	50	60	70	80	90
1,8-Cinéole	41.11	61.50	45.38	34.77	52.33	39.57	26.21
Globulol	18.08	8.66	19.81	22.75	21.27	24.71	27.57
Para-cymene	11.03	9.21	11.12	9.69	10.97	-	7.36
Phénol	3.70	-	2.18	2.67	-	2.74	-

temperature in 30°C. While for the temperatures 40, 50 and 70°C, the model of Henderson and Pabis is the best adapted while for 60°C Newton's model is the best.

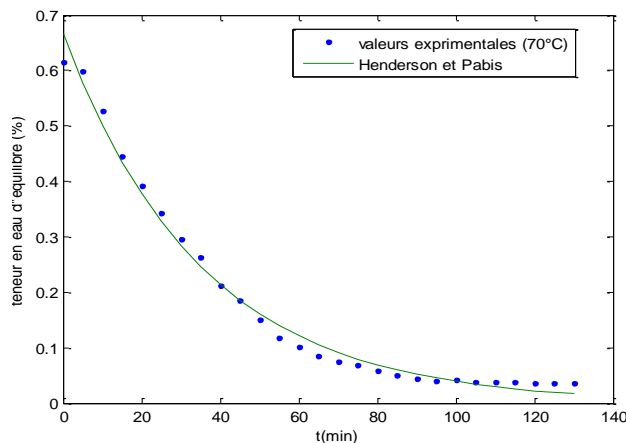
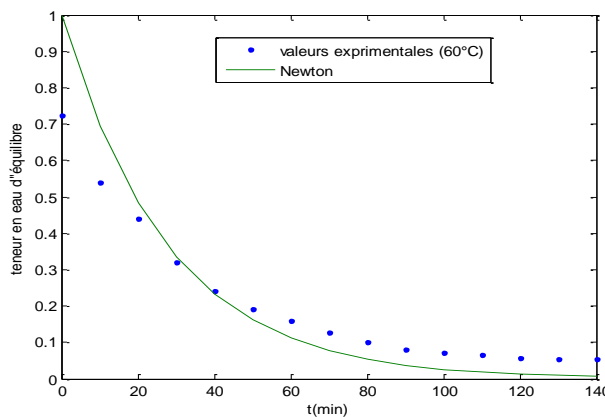
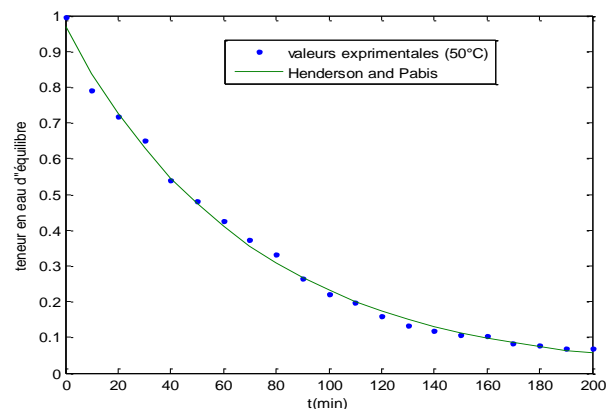
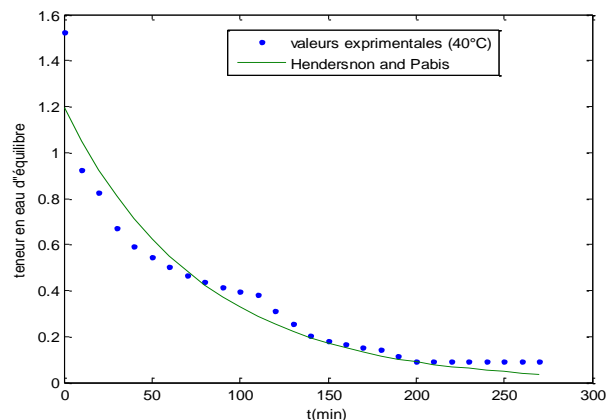
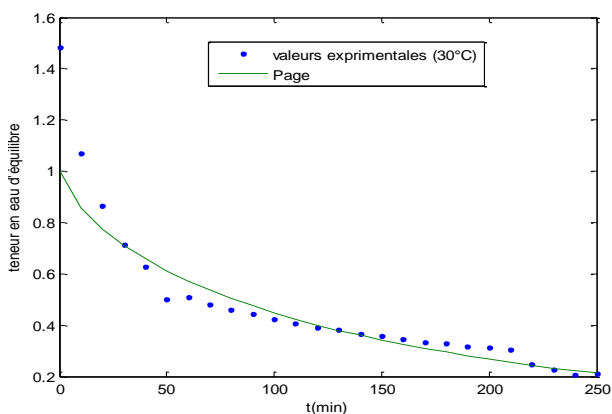


Fig 7: Curves of the kinetic modeling

3) Extraction of essential oil

The efficiency on extraction in oil the main things is defined as follows:

$$\% \eta_{HE} = \frac{\text{Mass of the Essential Oil in the organic phase} \times 100}{\text{Initial mass of the vegetable material dries}}$$

The effect of drying on the efficiency on extraction of the vegetable material of Eucalyptus Camaldulensis is presented on the figure 8.

According to this figure, we can deduct that the optimal temperature of drying is of 80°C because in this value of the temperature we obtained the highest efficiency The results of qualitative analysis show that the compound members of the majority party of it hey

obtained by hydrodistillation of *Eucalyptus Camaldulensis* are the 1,8_cinéole (61,5-26,21%) and the globulol (8,66-27,57%).

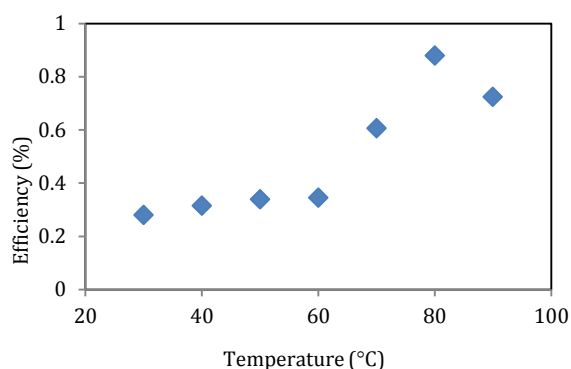


Fig 8: Influence of the temperature of drying on the efficiency on extraction of the essential oil

We can conclude that the optimal temperature to obtain the best quality of essential oil of *Eucalyptus Camaldulensis* is of 40°C.

Conclusion

This study confirms that the determination and the modeling of the isotherms of sorption and of the kinetics of drying establish an inescapable stage in any process of drying.

In order to understand better and arrest the problems connected to the preservation, to the experiment and to the modeling of the processes of drying, we should have a big knowledge of them.

From the obtained results, we can conclude that the model of GAB slanders well the isotherms of sorption for different temperature. We still note the presence of the phenomenon of hysteresis between the curves of adsorption and that of desorption. Then, the curves of the kinetics of drying show that the time of drying and the moisture content are inversely proportional to the temperature.

The results of the modeling of the kinetics of drying gave us that the model of Page, Henderson and Pabis and Newton describe well the kinetics of drying for the temperatures 30, (40, 50 and 70), 60°C respectively.

The experimental studies of extraction of essential oil from EC allowed us to recapitulate that the best efficiency is reached for an equal temperature in 80°C (0.879 %), and the best quality is obtained for an equal temperature of drying in 40°C.

It can be concluded that to manage economically the process of drying, we can now study the expenses in isosteric heat.

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